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13. ABSTRACT (maximum 200 words)

Our goal has been to develop experimental and theoretical methods capable of characterizing the structure and dynamics of molecules undergoing large amplitude vibrational motions and/or chaotic dynamics. We have made progress toward this goal using the Stimulated Emission Pumping technique combined with statistical pattern-recognition schemes. Our SEP study of HCP samples the HCP↔HPC isomerization barrier. Other spectroscopic results include: radiative lifetimes, self quenching rates, and electric dipole moment of HCN $\tilde{A}^1A''$; characterization of a new predissociated, low-barrier to linearity $\pi^{*2}\leftarrow\pi^2$ state of HCP; effect of heavy atom vibrations on intramolecular proton transfer in tropolone; and a vibronic coupling model for the isotopic, vibrational, and $J_{Ka,Kc}$ dependence of the electric dipole moment in the formaldehyde $\tilde{A}^1A_2$ state. Collisional energy transfer studies in the formaldehyde $\tilde{A}^1A_2$ state demonstrate a-dipole propensity rules for both J and M_J, $J_{Ka,Kc}$-dependent quenching rates in D_2CO $\tilde{A}$ v_4=1, and the absence of any low-pressure anomaly (beyond that due to rapid equilibration between the $\tilde{A}$ v_4=1 and v_4=0 vibrational levels) in the undispersed fluorescence from D_2CO $\tilde{A}$ v_4=1. We have developed three statistical pattern recognition techniques, Statistical Fourier Transform, Spectral Cross-Correlation, and Extended Autocorrelation, and applied these to experimental and computed spectra of HCN, HCP, acetylene, and NO_2.

14. SUBJECT TERMS Spectroscopy, Vibrational Structure, Molecular Dynamics, Large Amplitude Vibration, Isomerization, Quantum Chaos, Rotational Energy Transfer, Predissociation, Pattern Recognition, Tunneling

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F. Temps, S. Halle, P.H. Vaccaro, R.W. Field, and J.L. Kinsey, "Collisional Energy Transfer in Highly Vibrationally Excited H_2CO ($\tilde{X}\,^1A_1$)" J. Chem. Phys. 87, 1895-1897 (1987).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A. Spectroscopic Studies of HCN

Using 188nm tunable radiation generated by four wave mixing, fluorescence excitation spectra of $\tilde{A}^1A''$-$\tilde{X}^1\Sigma^+$ were recorded at the highest resolution achieved to date. Radiative lifetimes, self quenching rate coefficients, and electric dipole moments of several individual $\tilde{A}$-state rotation-vibration levels were measured. The HCN project was initiated with the goal of recording Stimulated Emission Pumping (SEP) spectra of highly vibrationally excited $\tilde{X}$-state HCN in order to study the onset of H-orbiting-CN isomerization resonances and the evolution from regular to chaotic dynamics. These experiments were discontinued when Professor A. Wodtke at the University of California Santa Barbara recorded SEP spectra of HCN using 10^3 and 10^2 times higher pulse energies in PUMP and DUMP lasers, respectively.

B. Spectroscopic Studies of HCP

HCP and HCN are homologous molecules. When we discontinued our study of HCN, we initiated experiments on HCP with the expectation that we would sample similar isomerization dynamics and order→chaos evolution. We have observed, by Stimulated Emission Pumping spectroscopy, an unprecedented long progression in pure overtones of the bending mode, extending up to $v_2'' = 42$ (25315 cm^{-1} above the zero point level). The evolution of the rotation-vibration molecular constants provide a detailed picture of the region near the top of the HCP↔HPC isomerization barrier (up to an HCP angle of only 30°, which corresponds to a turning point to turning point bending amplitude of 300°). The regularity of the spectrum at such high bending excitation is unexpected and completely different from the behavior revealed in Wodtke's SEP spectrum of HCN.

In addition to the downward SEP spectra, which sample the HCP $\tilde{X}^1\Sigma^+$ $v_2'' >> 0$ levels, upward Optical Optical Double Resonance (OODR) spectra of a predissociated $3^1A'$ state have been recorded. This state involves a $\pi^{*2}\leftarrow\pi^2$ double excitation relative to the HCP $\tilde{X}^1\Sigma^+$ state, and therefore has a C-P bond-order of 1 (in contrast to 3 in the $\tilde{X}$ state). These OODR spectra will permit us to determine the predissociation mechanism (from measured linewidths) and the shape of the relatively low barrier to linearity in the $3^1A'$ state.

C. Intramolecular Proton Transfer in Tropolone

A supersonic jet LIF apparatus was constructed in which fluorescence excitation spectra of tropolone and its ^{16}O, ^{18}O and H,D isotopomers were recorded. These spectra identify the heavy atom motions which accompany intramolecular proton transfer and clarify the mechanism whereby tunneling is suppressed or promoted by excitation of specific heavy atom vibrations.

Multiphoton Ionization detection capability has been added to the supersonic jet apparatus used for these tropolone experiments.

D. Energy Transfer Studies of Formaldehyde

The Transient Gain Spectroscopy (TGS) technique allowed us to complete three unique types of kinetic measurements on formaldehyde in the $\tilde{A}^1A_2\ 4^1$ vibronic level: (i) $J, M_J \rightarrow J', M_J'$ rate coefficients follow a-axis electric dipole propensity rules for both J and M_J (for H_2CO $\tilde{A}/H_2CO\ \tilde{X}$ self relaxation collisions), (ii) for D_2CO ($\tilde{A}$)/He collisions, there is a nonsystematic $J_{Ka,Kc}$-dependent variation of the fluorescence quenching rate, (iii) for undispersed fluorescence from the $D_2CO\ \tilde{A}\ 4^1$ level, the anomalous Stern-Volmer nonlinearities observed by Weisshaar and Moore at low pressure (< 10 mTorr) are shown to be the result of an experimental artifact, but the multiexponential fluorescence decay arises from reversible $\tilde{A}\ 4^1 \leftrightarrow 4^\circ$ vibrational relaxation. Observation (i) clarifies the mechanism of collision induced depolarization of an asymmetric top molecule, especially effects in the presence of an external electric field. Observation (ii) reflects collision induced coupling between S_1 rovibronic levels and the "lumpy continuum" of S_0, which is the D_2CO collisional counterpart of the strong $J_{Ka,Kc}$-dependence of the unimolecular decay rates in the $H_2CO\ \tilde{A}\ 4^0$ and 4^1 levels. Observation (iii) solves the last remaining mystery surrounding the long and controversial history of formaldehyde $\tilde{A}$-state photophysics.

E. Statistical Spectroscopy

At high vibrational excitation, rotation-vibration eigenstates of small polyatomic molecules cannot be assigned to a set of 3N-6 normal mode vibrational and 1 or 2 rotational projection quantum numbers. Without assignment, the structural and dynamical information encoded in the set of observable eigenstates cannot be utilized. We have applied or developed several statistically-based measures capable of extracting useful information from unassignable

spectra. These methods include $\langle |FT\ I(\omega)|^2 \rangle$ (the average of the square modulus of the Fourier transform of the spectrum, called the Statistical Fourier Transform (SFT)), Spectral Cross Correlation (SCC), and Extended Auto-Correlation (XAC). The SFT looks for systematic departures from chaotic-limit behavior, the SCC detects the loss of memory of a specific approximate partitioning of phase space, as would be produced by isomerization resonances; the XAC allows us to pick out fragments of regularity embedded in a chaotic manifold of levels by building a numerical filter based on *a priori* known level spacing and relative intensity patterns.

The development of statistical measures for decoding unassignable spectra has been the most important (and difficult) component of the research supported by AFOSR-88-0062.

AFOSR Program Manager: Larry P. Davis, Lt. Col., USAF
Dr. Francis J. Wodarczyk

B. Research Objectives

1. Apply the Stimulated Emission Pumping (SEP) technique to highly excited vibrational levels of a computationally tractable molecule such as HCN or HCP in order to understand how unimolecular isomerization and the evolution toward chaotic classical dynamics are encoded in an eigenstate spectrum.

2. Characterize barriers to intramolecular proton transfer in molecules, such as tropolone, in which the barrier to tunneling depends sensitively on vibrational excitations involving remote heavy atoms.

3. Apply multiple resonance PUMP/PROBE schemes to examine collision induced energy transfer processes in formaldehyde with a goal of explaining paradoxical prior observations from other laboratories.

4. Develop statistical measures capable of extracting useful information from unassignable spectra of vibrationally highly excited molecules.

5. Use SEP to prepare a specific rotation-vibration level of a reactant in order to characterize the effect of vibrational excitation on the rate and product branching ratio of a reaction such as NH_2 (v, $J_{K_aK_c}$) + O_2.

C. Status of Research Effort

Significant progress toward all but the last of the cited objectives has been made.

Technical Progress Report -- 1 November 1987 - 31 October 1990

1. SEP Studies for Computationally Tractable Molecules

Quantum mechanics encodes information about simple classical ball-and-spring motions into an eigenstate spectrum. At high excitation energy, when the classical dynamics is chaotic and bond-rearrangement (i.e., isomerization) processes occur, the spectrum becomes unassignable [1-3] and none of the information contained in it is accessible via traditional pattern-recognition techniques. A central theme of our AFOSR-supported research has been development of new methods for extracting information about chaotic dynamics [4] and large amplitude motions [5] from unassignable spectra.

Triatomic monohydride molecules are special because they are the simplest molecular systems capable of both isomerization and chaos; they are also just barely within reach of modern, supercomputer-based schemes for computing a rotation-vibration spectrum from a potential energy surface (and possibly *vice versa*) [6-9]. In addition, accurate triatomic monohydride potential surfaces are starting to become available from experimentally calibrated *ab initio* calculations. Therefore, we expect to be able to examine the viability of spectrum-to-potential inversion schemes and to test the validity of conclusions drawn from nontraditional, statistically-based pattern-recognition schemes against both computed spectra of a known potential surface and experimental spectra of an incompletely known surface.

Obviously, HCN is the ideal molecule for any advance on this fundamental problem of molecular structure and dynamics. A significant fraction of our effort was invested in what ultimately proved to be an unsuccessful effort to record Stimulated Emission Pumping (SEP) spectra of HCN via the moderately predissociated $\tilde{A}^1A''$ state. The PUMP step of SEP required tunable VUV radiation generated by four wave mixing in Sr vapor [10, 11]. The four wave mixing scheme required two tunable dye lasers. The DUMP step of SEP required a frequency doubled dye laser. Our strategy was to pump all three dye lasers by a single 400mJ/pulse excimer laser. Based on our experience with SEP spectra of the homologous HCCH molecule via the corresponding $\tilde{A}^1A_u$ state, we were confident that the necessary PUMP and DUMP intensities could be generated by this scheme. We were rather quickly able to record high resolution HCN $\tilde{A}\leftarrow\tilde{X}$ fluorescence excitation spectra [10], but SEP spectra eluded us despite valiant efforts by Dave Jonas, Kaoru Yamanouchi, and Xinsheng Zhao. The reason for our failure became evident when Alec Wodtke at UCSB was able to record SEP spectra of HCN using a different experimental scheme [12]. His PUMP laser was a tunable ArF excimer [13], which generated 10^3 times the pulse energy of our four wave mixing scheme. More importantly, his DUMP step, which utilized a doubled dye laser pumped by the full output of a second (XeCl) excimer laser, generated 10^1 to 10^2 times the pulse energy of our doubled dye laser pumped by less than 1/3 of the power of our single excimer laser. It turned out that the oscillator strength of the HCN $\tilde{A}$-$\tilde{X}$ system was ~10 times smaller than that of the corresponding HCCH $\tilde{A}$-$\tilde{X}$ system! We therefore abandoned our HCN SEP project in favor of HCP.

The HCP SEP spectrum (Yit-Tsong Chen, Kevin Lehmann, David Watt, Yasuhiro Ohshima, King-Chuen Lin), recorded via the $\tilde{A}^1A''$ state, consists exclusively of strong transitions involving the (0, v_2, 0) and 0, v_2, 1) vibrational levels of the $\tilde{X}^1\Sigma^+$ state, where v_2 is the bend and v_3 is the CP stretch [14]. Up to $v_2 = 30$, the spectrum is surprisingly regular,

despite the large amplitude, curvillinear motion implied by such high overtones of a bending vibration. In the $30 < v_2 \leq 42$ region, the SEP spectrum shows unmistakable signs of HCP↔HPC isomerization, but retains sufficient regularity to be at least partially assigned and deperturbed. When the $\tilde{C}^1A'$ state is used as the SEP intermediate state, we observe no selectivity toward the pure bend overtones, and the observed density of vibrational states is consistent with the computed total density of $\ell = 0$ vibrational states. Thus, near the top of the isomerization barrier, we are able to observe selectively either assignable pure overtone levels or *all* (probably unassignable) vibrational levels depending on whether we use the $\tilde{A}$ or $\tilde{C}$ state as the SEP intermediate. We are preparing to record SEP spectra of DCP (Yit-Tsong Chen, John Wang). The stability and Franck-Condon observability of the high bending overtones are surprising and, at present, inexplicable.

In order to understand the SEP spectra of HCP, we are initiating collaborations with various research groups. Theresa Kavanaugh spent several months at the Institute for Molecular Science (Okazaki, Japan) and initiated a collaboration with Dr. K. Yamashita on *ab initio* calculations of the HCP $\tilde{X}^1\Sigma^+$ state potential surface. We have sent our SEP data to Professor Ian Mills (Reading, U.K.) who is fitting it by a scheme that proved uniquely successful for HCN [9]. We (David Chasman, Theresa Kavanaugh, David Jonas) have applied statistical measures to computed SEP spectra of HCN provided by R. Wyatt (Texas) and C. LeForestier (Orsay, France) [7]. We (David Yaron, Theresa Kavanaugh) are using Semi-Rigid-Bender programs provided by Dr. P. Bunker (NRC Ottawa, Canada) [15, 16] to fit our HCP bending progression data. We expect to send our HCP, DCP data set to Michael Kellman (Oregon) to be fitted by his "Bootstrap" method [8]. Zlatko Bačić (NYU) [6] will perform variational DVR-DGB calculations on the improved HCP $\tilde{X}$-state potential surface in order to help us to assign the dominant perturbers of the bending overtone levels and to explain the stability and Franck-Condon observability of the $(0, v_2, 0)$ levels.

Interspersed among the sharp downward SEP transitions are broad upward OODR transitions into the previously unobserved $\pi^{*2}\leftarrow\pi^2\ 3^1A'$ state which is the subject of a recent *ab initio* calculation by P. Bruna et al [17]. Our (Yit-Tsong Chen, Steve Coy) analysis of this system will characterize the low barrier to linearity and the mechanism of predissociation of the $3^1A'$ state.

2. Barriers to Intramolecular Proton Transfer

Tropolone is an example of an internally hydrogen bonded molecule in which an intramolecular hydrogen transfer between oxygen atoms leads to a chemically identical species. What makes tropolone especially interesting is that the hydrogen transfer requires small displacements of several heavy (carbon) atoms remote from the center of the large amplitude (hydrogen) motion. Our (Richard Redington, Bhavani Rajaram) study of the $\tilde{A}^1B_2$ state of tropolone has revealed extreme vibrational mode specificity in the tunneling rates between tautomers [18]. The nature of the tunneling coordinate has been clarified by systematic isotopic substitution ($^{16}O_2$, $^{16}O\,^{18}O$, $^{18}O_2$; H, D) and normal coordinate analyses of an *ab initio* potential surface [19].

We had initially hoped to record SEP spectra of tropolone, so that tunneling on the $\tilde{X}^1A_1$ potential surface could be systematically studied. This goal has so far eluded us because multiphoton processes driven by the $\tilde{A}\leftarrow\tilde{X}$ PUMP laser prevent buildup of significant population in the $\tilde{A}$-state [20]. We have installed a primitive MPI detector in our supersonic jet LIF apparatus and are exploring the possibility of detecting SEP by the ionization-dip rather than the fluorescence-dip scheme that has so far been the exclusive basis for all of our SEP studies.

3. Collisional Studies of H_2CO and D_2CO in the $\tilde{A}^1A_2$ State [21]

The Transient Gain Spectroscopy (TGS) technique allowed us to complete three unique types of kinetic measurements on formaldehyde in the $\tilde{A}^1A_2\,4^1$ vibronic level: (i) $J, M_J \rightarrow J', M_J'$ rate coefficients follow a-axis electric dipole propensity rules for both J and M_J (for H_2CO $\tilde{A}/H_2CO\,\tilde{X}$ self relaxation collisions), (ii) for D_2CO ($\tilde{A}$)/He collisions, there is a nonsystematic $J_{Ka,Kc}$-dependent variation of the fluorescence quenching rate, (iii) for undispersed fluorescence from the $D_2CO\,\tilde{A}\,4^1$ level, the anomalous Stern-Volmer nonlinearities observed by Weisshaar and Moore at low pressure (< 10 mTorr) are shown to be the result of an experimental artifact, but the multiexponential fluorescence decay arises from reversible $\tilde{A}\,4^1\leftrightarrow 4^0$ vibrational relaxation. Observation (i) clarifies the mechanism of collision induced depolarization of an asymmetric top molecule, especially effects in the presence of an external electric field. Observation (ii) reflects collision induced coupling between S_1 rovibronic levels and the "lumpy continuum" of S_0, which is the D_2CO collisional counterpart of the strong $J_{Ka,Kc}$-dependence of the unimolecular decay rates in the $H_2CO\,\tilde{A}\,4^0$ and 4^1 levels. Observation (iii) solves the last

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5. SEP Preparation of State Selected Reactants

After detailed study of the proposed NH_2 $\tilde{X}(v, J_{Ka,Kc})$ + O_2 reactive SEP experiment, both James Lundberg and George Adamson concluded that the difficulties were prohibitive. They selected other nonreactive SEP experiments (HCO $\tilde{X}^2A'$ and DCCD triplet states, supported by a DOE grant).

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19. R.L. Redington, T.E. Redington, M.A. Hunter, and R.W. Field, "$\tilde{A}^1B_2$-$\tilde{X}^1A_1$ 26_0^v Transitions of ^{18}O-Enriched Tropolone", J. Chem. Phys. 92, 6456-6462 (1990); and R.L. Redington, J. Chem. Phys. 92, 6447 (1990).

20. R.L. Redington and R.W. Field, "Laser Fluorescence Excitation Band Profiles of Jet-Cooled Tropolone", Spectrochim. Acta 45A 41-46 (1989).

21. S. Halle, Ph.D. Thesis, MIT 1989.

D. Cumulative List of Publications Resulting from AFOSR Supported Research (since 1982)

R.F. Marks, R.A. Gottscho, and R.W. Field, "The CaO D,d$^{1,3}\Delta$-a$^3\Pi$ System: Sub-Doppler Spectrum, Rotational Analysis, and Deperturbation", Physica Scripta 25, 312-328 (1982).

R.F. Marks, H.S. Schweda, R.A. Gottscho, and R.W. Field, "The Orange Arc Bands of CaO: Analysis of a D,d$^{1,3}\Delta$-a$^3\Pi$ System", J. Chem. Phys. 76, 4689-4691 (1982).

D.E. Reisner, P.H. Vaccaro, C. Kittrell, R.W. Field, J.L. Kinsey and H.-L. Dai, "Selective Vibrational Excitation of Formaldehyde $\tilde{X}^1A_1$ by Stimulated Emission Pumping", J. Chem. Phys. 77, 573-575 (1982).

H.L. Dai, E. Abramson, R.W. Field, D. Imre, J.L. Kinsey, C.L. Korpa, D.E. Reisner, and P.H. Vaccaro, "Single Eigenstate Polyatomic Molecule Vibrational Spectroscopy at 1-4eV", Springer Series Opt. Sci. 40, 74-77, (1983).

P.H. Vaccaro, J.L. Kinsey, R.W. Field, and H.-L. Dai, "Electric Dipole Moments of Excited Vibrational Levels in the $\tilde{X}^1A_1$ State of Formaldehyde by Stimulated Emission Spectroscopy," J. Chem. Phys. 78, 3659-3664 (1983).

F. Martin, S. Churassy, R. Bacis, R.W. Field, and J. Vergès, "Long Range Behavior of the Gerade States Close to the $^2P_{3/2} + {}^2P_{3/2}$ Iodine Dissociation Limit by Laser-Induced Fluorescence Fourier-Transform Spectroscopy", J. Chem. Phys. 79, 3725-3737 (1983).

Li Li and R.W. Field, "Direct Observation of High-Lying $^3\Pi_g$ States of the Na_2 Molecule by Optical-Optical Double Resonance," J. Phys. Chem. 87, 3020-3022 (1983).

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E. Abramson, H.-L. Dai, R.W. Field, D.G. Imre, J.L. Kinsey, C. Kittrell, D.E. Reisner, and P.H. Vaccaro, "Laser Population of Highly Excited Vibrational Levels of Molecules," Reactants and Probes in Chemistry, W.M. Jackson and A.B. Harvey, eds. pp. 393-404 Howard University Press, 1985.

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H.-L. Dai, R.W. Field, and J.L. Kinsey, "State-Specific Rates of $H_2CO(S_0) \rightarrow H_2 + CO$ at Energies Near the Top of the Barrier: A Violation of RRKM Theory?", J. Chem. Phys. 82, 1606-1607 (1985).

H.-L. Dai, R.W. Field, and J.L. Kinsey, "Intramolecular Vibrational Dynamics Including Rotational Degrees of Freedom: Chaos and Quantum Spectra", J. Chem. Phys. 82, 2161-2163 (1985).

P.H. Vaccaro, R. Redington, J. Schmidt, J.L. Kinsey, and R.W. Field, "Rotational Relaxation in the H_2CO $\tilde{A}\,^1A_2$ State by Transient Gain Spectroscopy", J. Chem. Phys. 82, 5755-5756 (1985).

G. Pichler, J.T. Bahns, K.M. Sando, W.C. Stwalley, D.D. Konowalow, Li Li, R.W. Field, and W. Müller, "Electronic Assignments of the Violet Bands of Sodium", Chem. Phys. Lett. 129, 425-428 (1986).

C.E. Hamilton, J.L. Kinsey, and R.W. Field, "Stimulated Emission Pumping: New Methods in Spectroscopy and Molecular Dynamics," Ann. Rev. Phys. Chem. 37, 493-524 (1986).

F. Temps, S. Halle, P.H. Vaccaro, R.W. Field, and J.L. Kinsey, "Collisional Energy Transfer in Highly Vibrationally Excited H_2CO ($\tilde{X}\,^1A_1$)" J. Chem. Phys. 87, 1895-1897 (1987).

P.H. Vaccaro, F. Temps, S. Halle, J.L. Kinsey, and R.W. Field, "Polarization-Detected Transient Gain Studies of Relaxation Processes in $v_4 = 1$ $\tilde{A}\,^1A_2$ Formaldehyde-h_2", J. Chem. Phys. 88, 4819-4833 (1988).

R.L. Redington, Y. Chen, G.J. Scherer, and R.W. Field, "Laser Fluorescence Excitation Spectrum of Jet-Cooled Tropolone: The $\tilde{A}^1B_2$ - $\tilde{X}^1A_1$ System", J. Chem. Phys. 88, 627-633 (1988).

F. Temps, S. Halle, P.H. Vaccaro, R.W. Field, and J.L. Kinsey, "Vibrationally Excited Formaldehyde: The Relationship between Vibrational Structure and Collisional Properties", Faraday Discussion on Molecular Vibrations, 1987, J. Chem. Soc. Faraday Trans. 2, 84, 1457-1482 (1988).

R.W. Field, "High Resolution Spectroscopy of Small Molecules", Conference Laser M2P, 1987, J. de Physique C7, 17-28 (1987).

M.H. Alexander, P. Andresen, R. Bacis, R. Bersohn, F.J. Comes, P.J. Dagdigian, R.N. Dixon, R.W. Field, G.W. Flynn, K.-H. Gericke, B.J. Howard, J.P. Huber, D.S. King, J.L. Kinsey, K. Kleinermanns, A.C. Luntz, A.J. MacCaffery, B. Pouilly, H. Reisler, S. Rosenwaks, E. Rothe, M. Shapiro, J.P. Simons, R. Vasudev, J.R. Wiesenfeld, C. Wittig, and R.N. Zare, "A Nomenclature for Λ Doublet Levels in Rotating Linear Molecules", J. Chem. Phys. 89, 1749-1753 (1988).

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P.H. Vaccaro, A. Zabludoff, M. Carrera-Patiño, J.L. Kinsey, and R.W. Field, "High Precision Dipole Moments in $\tilde{A}\,^1A_2$ Formaldehyde Determined via Stark Quantum Beat Spectroscopy", J. Chem. Phys. 90, 4150-4167 (1989).

R.W. Field, "Pathologically Complex Spectra of Small Molecules: High Resolution Techniques for Displaying Vibrational Chaos and Electronic Simplicity", Conference on Quantum Electronics and Laser Science, 1989 Technical Digest Series, Vol. 12 (Optical Society of America, Washington, DC), pp. 160-162 (Talk THHH2), 1989.

R.W. Field, "Statistical Spectroscopy: Insight or Nonsense?", ILS-IV, 1988, Am. Instit. of Phys. Conf. Proc. 191, 673-682 (1988).

F. Temps, S. Halle, P.H. Vaccaro, R.W. Field, and J.L. Kinsey, "Collisional Relaxation of H_2CO ($\tilde{A}\,^1A_2$, $v_4 = 1$, $J_{Ka,Kc} = 13_{2,12}$) by He, Ar, Xe, and N_2", J. Chem. Phys. 91, 1008-1011 (1989).

D.M. Jonas, X. Zhao, K. Yamanouchi, P.G. Green, G.W. Adamson, and R.W. Field, "High Resolution VUV Fluorescence Excitation and Predissociation of $\tilde{A}^1A''$ HCN", J. Chem. Phys. 92, 3988-3989 (1990).

R.L. Redington, T.E. Redington, M.A. Hunter, and R.W. Field, "$\tilde{A}^1B_2$-$\tilde{X}^1A_1$ 26_0^v Transitions of ^{18}O-Enriched Tropolone", J. Chem. Phys. 92, 6456-6462 (1990).

Y.-T. Chen, D.M. Watt, R.W. Field, and K.K. Lehmann, "Observation of Highly Vibrationally Excited $\tilde{X}^1\Sigma^+$ HCP by Stimulated Emission Pumping Spectroscopy", J. Chem. Phys. 93, 2149-2151 (1990).

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D.M. Jonas, "Spin Statistics: An Error in Landau and Lifschitz' Quantum Mechanics", J. Chem. Phys. 90, 5563-5565 (1989).

S.L. Coy, R. Hernandez, and K.K. Lehmann, "Limits on the Transition to Gaussian Orthogonal Ensemble Behavior: Saturated Radiationless Transitions Between Strongly Coupled Potential Surfaces", Phys. Rev. A. 40, 5935-5949 (1989).

E. Personnel

1. Visiting Scientists

Professor King-Chuen Lin (HCP)
National Taiwan University

Dr. Yasuhiro Ohshima (HCP)
University of Tokyo

Dr. Jean-Paul Pique (Statistical Fourier Transform)
University of Grenoble

Professor Richard Redington (Tropolone)
Texas Tech University

Dr. Kaoru Yamanouchi (HCN)
University of Tokyo

2. Postdoctoral Associates

Dr. Yit-Tsong Chen (HCP)

Dr. Stephen L. Coy (Formaldehyde energy transfer, chaos, extended autocorrelation)

Dr. Friedrich Temps (Formaldehyde energy transfer)

Dr. Xinsheng Zhao (HCN)

3. Graduate Students

George Adamson (HCN)
David Chasman (chaos, extended autocorrelation)
Yongqin Chen (spectral cross correlation)

Peter Green (HCN)
Scott Halle (Formaldehyde energy transfer)
David Jonas (HCN, spectral cross correlation, chaos)
Theresa Kavanaugh (statistical measures, HCP *ab initio*)
Bhavani Rajaram (Tropolone)
Stephani Solina (HCN dipole moment)
David Watt (HCP)

4. Undergraduate Students

Martin Hunter (Tropolone)

F. Interactions: Spoken papers (since 1986)

2/25/86 University of California, Berkeley, Physical Chemistry Seminar, "Spectroscopy of Vibrationally Highly Excited Molecules: Toward a Time Dependent View of Quantum Ergodicity."

2/26/86 University of California, Berkeley, Chemical Dynamics Seminar "Vibrationally Hot Formaldehyde: Is There Any Connection Between Spectroscopic and Collisional Properties?"

2/28/86 The Aerospace Corporation, "Spectroscopy of Vibrationally Highly Excited Molecules: Toward a Time Dependent View of Quantum Ergodicity."

3/3/86 Brandeis University, Department of Chemistry, "Vibrationally Hot Acetylene and Formaldehyde: Techniques, A Quiz, and the Case of the Missing δ-Levels."

3/6/86 Cornell University, Department of Chemistry, "Spectroscopy of Vibrationally Highly Excited Molecules: Toward a Time Dependent View of Quantum Ergodicity."

3/7/86 State University of New York, Buffalo, Department of Chemistry, "Vibrationally Hot Acetylene: What is Quantum Ergodicity Anyway?"

3/17/86 - 3/21/86 University of Texas, Austin, Department of Chemistry, Distinguished Visiting Lecturer

"The Evolution from Trivally Assignable to Intrinsically Unassignable Spectra: From RKR to RRKM."

"Quantum Ergodicity: Time Scales, What is Accessable?, and Collisions."

"Stark and Zeeman Quantum Beat Spectroscopy of Formaldehyde and Acetylene."

"Tunneling in Li_2, Na_2, H_2CO, and HCCH."

4/14/86 Rutgers University, Department of Chemistry, "Missing Levels in Vibrationally Hot Acetylene."

4/17/86 Iowa State University, Department of Chemistry, "Vibrationally Hot Acetylene: Quantum Chaos, Isomerization, and Spectroscopic Mysteries."

8/12/86 Gordon Conference on Vibrational Spectroscopy, Wolfeboro, Invited talk, "Dynamical Information from Intrinsically Unassignable High Resolution Spectra."

9/3/86 Massachusetts Institute of Technology, Chemical Sciences/Industry Forum: Lasers and Chemistry...The State of the Art, "From Quantum Quantum Beats to Triple Resonance but What on Earth For?"

10/16/86 AFOSR Contractor's Meeting, Dr. F. Temps, "Rotational Energy Transfer in the H_2CO $\tilde{A}^1A_2$ and $\tilde{X}^1A$ states

4/6-8/87 Poster sessions by research group members at 193rd, American Chemical Society National Meeting, Denver, Colorado:

S. Halle (#114) "Collisional Energy Transfer in Highly Vibrationally Excited H_2CO $\tilde{X}^1A_1$)."

Y. Chen (#117) "A Spectroscopic Study of Acetylene↔Vinylidene Isomerization."

C.E. Hamilton (118) "Local Bending Vibrations in the $\tilde{A}^1A''$ and $\tilde{X}^1\Sigma$ States of Monodeuterated Acetylene."

4/21/87 Joint Institute for Laboratory Astrophysics, "Acetylene: Dissociation, Isomerization, and Quantum Chaos."

5/4/87 Ohio State University, Department of Chemistry, "Acetylene: Dissociation, Isomerization, and Quantum Chaos."

6/4/87 Department of Energy, Contractors' Meeting, "Spectroscopic Studies of Acetylene."

7/3/89 Université de Grenoble, Department of Physics, "Acetylene: Dissociation, Isomerization, and Quantum Chaos."

7/7/89 Laser M2P Lyon, Invited talk, "High Resolution Spectroscopy of Small Molecules."

8/19/87 Bunsengesellschaft Meeting on Intramolecular Processes, Grainau, Germany, Invited talk, "Acetylene: Isomerization and Dissociation."

9/11/87 USC Symposium on Chemistry and Photophysics of Energetic Species, Invited talk, "Acetylene: Isomerization and Dissociation."

10/14/87 University of Washington, Department of Chemistry, "Acetylene: Isomerization, Dissociation, and Chaos."

11/16/87 MIT, Symposium in Honor of Professor J. L. Kinsey, "Chaos Out of Order: The Kinsey Effect."

11/23/87 Oak Ridge National Laboratory, Chemistry Division, "Acetylene: Isomerization, Dissociation, and Chaos."

12/1/87 National Bureau of Standards, Molecular Spectroscopy Division, "Acetylene: Dissociation, Isomerization, and Quantum Chaos."

12/16/87 Faraday Symposium on Molecular Vibrations, Reading, England, Invited talk, F. Temps. "Vibrationally Excited Formaldehyde: The Relationship between Vibrational Structure and Collisional Properties."

3/22/88 American Physical Society, 2 Invited talks, New Orleans, Plyler Prize, "Symmetry Pre-Sorted Spectra of Vibrationally Excited Acetylene: Statistical Analyses of Intrinsincally Unassignable Spectra" and "A Zero-Order Model for the Electronic Structure of Diatomic Molecules: Periodicity, Localization, Supermultiplets, and Other Heresies."

4/11/89 University of Wisconsin, Department of Chemistry, "Statistical Spectroscopy: Insight or Nonsense?"

8/1/88 University of Maine, New England Regional Meeting, American Chemical Society, Invited talk, "Statistical Spectroscopy: Insight or Nonsense?"

10/4/88 International Laser Symposium-IV, Atlanta, Invited talk, "Statistical Spectroscopy: Insight or Nonsense?"

11/1/88 AFOSR Contractors' Meeting, Newport Beach, "Symmetry Pre-Sorted Spectra of Vibrationally Excited Acetylene: Statistical Analyses of Intrinsically Unassignable Spectra."

1/10/89 Informal Photochemistry Conference, USC, Invited talk, "Statistical Spectroscopy: Information from Intrinsically Unassignable Pure Sequence Spectra."

1/23/89 Argonne National Laboratory: Chemistry Colloquium, "Statistical Spectroscopy Information from Intrinsically Unassignable Pure Sequence Spectra."

1/24/89 Argonne National Laboratory: Chemical Dynamics Colloquium, "Three Mysteries: Two Explained, One Unveiled."

3/7/89 Institute for Molecular Science, Symposium on Highly Excited Molecules, Okazaki, Japan, Plenary lecture, "Intrinsically Unassignable Vibrational Spectra: SEP, Statistics, and Dynamics."

3/21/89	MIT-Modern Optics & Spectroscopy, "Statistical Spectroscopy: Information from Unassignable Spectra."
4/27/89	Quantum Electronics and Laser Spectroscopy (QELS), Baltimore, Invited talk, "Pathologically Complex Spectra of Small Molecules: High Resolution Techniques for Displaying Vibrational Chaos and Electronic Simplicity."
6/12/89	International Symposium on Molecular Spectroscopy, Ohio State University, Plenary lecture, "Intrinsically Unassignable Vibrational Spectra: SEP, Statistics, and Dynamics"
	Yit-Tsong Chen, Talk TH2 "An Isotopic Substitution test for Orbiting H Atoms in Vibrationally Highly Excited Acetylene"
	I. K. Lundberg, Talk TH3 "UV Optical Double Resonance Study of the Predissociated $\tilde{C}^1A_g$ State of Acetylene"
6/27/89	Future Trends in Spectroscopy, Vatican Symposium Commemorating 50th Anniversary of Spectrochimica ACTA, Invited talk, "Spectroscopy Beyond Molecular Constants."
7/11/89	Gordon Conference on Molecular Energy Transfer, Wolfeboro, Invited talk, "Information from Unassignable, Pure Sequence, SEP Spectra."
10/10/89	Tri-Joint Seminar, UCLA-CalTech-USC (at UCLA), "Information from Intrinsically Unassignable Spectra".
12/1/89	New York University, Department of Chemistry, "Information from Intrinsically Unassignable Spectra"
1/23/90	University of Toronto, Ontario Laser and Lightwave Center, "Information from Intrinsically Unassignable Spectra".
4/2-13/90	Joint Institute for Laboratory Astrophysics, JILA Distinguished Visitor, "Information from Intrinsically Unassignable Rotation-Vibration Spectra of Small Polyatomic Molecules "
4/23-27/90	199th American Chemical Society National Meeting, Boston, Co-Organizer (with Phil Pechukas) of Symposium on Large Amplitude Motions in Vibrationally Excited Molecules, Invited talk "Acetylene↔Vinylidene Isomerization: Tunneling Resonances in Eigenstate Resolved Spectra".
	Nobel Laureate Signature Award Prize Talk by Yongqin Chen, "Acetylene↔Vinylidene Isomerization".
5/8/90	University of California, Berkeley, Physical Chemistry Colloquium, "Information from Intrinsically Unassignable Spectra"
5/10/90	University of California, Santa Barbara, Department of Chemistry, "SEP Spectroscopy of Acetylene and HCP".

6/11-15/90 Symposium on Molecular Spectroscopy, Ohio State University Invited Talk, "Stark and Zeeman Anticrossing Spectroscopy of Acetylene $\tilde{A}^1A_u$"

9/19-21/90 International Laser Symposium (ILS-VI) Minneapolis, Invited talk, "Pure Sequence Vibrational Spectra above 2eV"

10/30/90 AFOSR Contractor's Meeting, Annapolis, "Assignable SEP Spectra Near the Top of the S_0 HCP↔HPC Barrier".

10/31/90 University of Rochester, Chemistry Departmental Colloquium, "Dynamics Encoded in Eigenstate and Continuum Spectra".

11/28/90 Indiana University, Department of Chemistry, DuPont Distinguished Lecture, "Dynamics Encoded in Spectra of Eigenstates and Resonances".

3/7/91 University of Pennsylvania, Physical Chemistry Seminar, "Dynamics Encoded in Eigenstates and Resonances".

3/28/91 Pennsylvania State University, "Dynamics Encoded in Eigenstate and Continuum Spectra".

4/19/91 American Chemical Society, Atlanta, Invited talk, "Dynamics Encoded in Spectra of Eigenstates and Resonances"

4/22-25/91 American Physical Society, Washington, DC, Invited talk, "Acetylene: Assignments Amongst the Unassignable".

7/2-5/91 7th International Congress of Quantum Chemistry, Menton, France, Invited talk.

G. Patents

None.